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Test Structures for the Characterisation of Conductive Carbon Produced from Photoresist

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Abstract— Conductive carbon films are highly attractive for use as electrodes in electrochemistry and biosensing applications. Patterned photoresist films can be transformed into carbon electrodes using standard photolithographic techniques followed by pyrolysis of the photoresist in a furnace under a reducing atmosphere. Previous studies have been made of the electrical properties of blanket carbon films created using this method of fabrication. However, there is a need to investigate pattern dependent effects, particularly the extent to which the dimensions of the patterned films shrink during the high temperature processing. This study applies microfabricated test structures to the process characterisation of conductive carbon produced from standard positive photoresists.

Keywords— Test Structures, Carbon, Electrochemistry.

I. INTRODUCTION

Carbon is a versatile and inexpensive electrode material that has the advantages of a wide anodic potential window, low electrical resistance and residual currents, and relatively inert electrochemistry, which accounts for its successful use in a wide range of biochemical and medical sensors [1-3]. As a result, the capability to deposit and pattern this material on integrated circuits has many attractions. One approach to achieving this is to expose and develop photoresist and then pyrolyse the resulting layer to form a patterned conductive carbon film [4]. This paper reports on the application of test structures as part of the process to characterise and develop the technology. Silicon wafers patterned with the test structure designs in photoresist are subjected to high temperature furnace processing in a reducing atmosphere. Two types of positive photoresist with different thicknesses have been characterised at two furnace temperatures. Standard sheet resistance measurements using Greek cross structures have been applied to study the variation of material conductivity. The thickness has also been characterised using surface profilometry to identify shrinkage and reflow of the material during pyrolysis. In addition, the electrochemical properties of carbon electrodes have been studied using a typical reduction/oxidation reaction.

II. TEST STRUCTURES AND MEASUREMENTS

A. Initial Process Development (Test Mask Design 1)

A number of different test structure designs have been used in the development and characterisation of the conductive carbon films. In the first stage of the project the focus was on developing the carbonisation furnace process to produce a uniform carbon coating across a 75mm diameter silicon wafer. Fig. 1 shows a wafer patterned with Test Mask Design 1, which consisted mainly of arrays of squares with a small number of electrical test structures in the positions indicated by the numbered ovals.

The photoresist used in these initial experiments was Microposit SPR350 with a nominal thickness of 2.2 μm . The pattern was exposed using a Karl Suss MA8 mask aligner and developed using the photoresist manufacturer's recommended processes. The furnace recipe used to pyrolyse the photoresist is detailed below, where the gas mixture and target temperature has been varied.

1. Load wafers at 30 °C, under nitrogen flow.
2. Ramp temperature up to target at 5 °C/minute
3. Hold at target temperature for 1 hour with desired gas mixture
4. Ramp temperature down to 30°C at 1 °C/minute, under nitrogen flow

Initial experiments used nitrogen gas flow at all stages but this was found to give poor results including complete or partial removal of photoresist. The wafer in Fig. 1 was produced in a reducing atmosphere at 950 °C, using forming gas (96% N₂, 4% H₂) during step 3. The final thickness of the carbon layer, measured with a Dektak surface profiler, was ~400 nm across the wafer, indicating shrinkage of about 82%. Best results were obtained by placing the product wafer vertically in the middle slot of a quartz wafer boat with 16 dummy wafers in adjacent slots, i.e., 8 on each side.

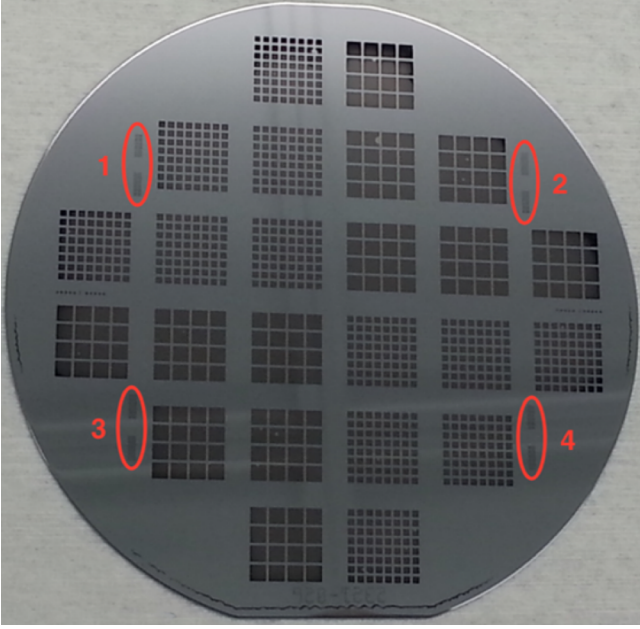


Fig. 1. Test structure wafer design used in initial experiments. Greek Cross and cross-bridge electrical test structure arrays are circled in red.

Fig. 2 shows a box-cross test structure printed using mask design 1, taken from the initial test wafer. The image suggests significant reflow and distortion of the photoresist during pyrolysis into conductive carbon.

B. Test Structure Mask Design 2.

As mask design 1 only had four pairs of cross bridge structures per wafer, a second design was used which included many more sets of sheet resistance and linewidth structures. This design (Mask 2) was originally used in work reported at ICMTS 2015 [5], and includes 32 sets of Greek cross structures located at the numbered sites identified in Fig. 3. Using this design, two wafers were prepared using SPR350 with a thickness of 2.2 μm and two with Microposit SPR220 with a thickness of 8.4 μm . One wafer of each thickness was carbonized at 950 $^{\circ}\text{C}$ and one at 1100 $^{\circ}\text{C}$.

Figure 4 shows a cross-bridge linewidth structure from a wafer patterned using mask design 2. This test structure design should enable both electrical linewidth and sheet resistance measurements [6]. However, the voltage tap connections to the bridge resistor showed significant narrowing which caused breaks in the conducting material. Hence, it was not possible to measure the bridge structure and so only sheet resistance measurements were made. It should be noted that the reflow of the resist evident in the centre of the Greek cross structure will make the sheet resistance measurement unrepresentative of the value in the bridge section of the structure. Further work is required to investigate the pattern dependent changes in these test structures.

C. Test Structure Mask Design 3

It was clear from the results using mask design 2 that a full wafer map of the resistance variation would be desirable. The design selected (Mask 3) was originally created for the characterisation of thick magnetic films [7].

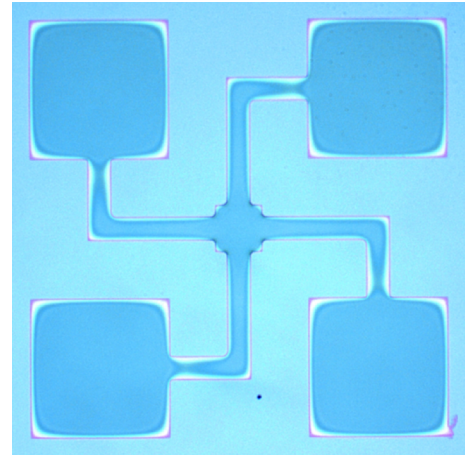


Fig. 2. Box cross sheet resistance test structure from test wafer design 1.

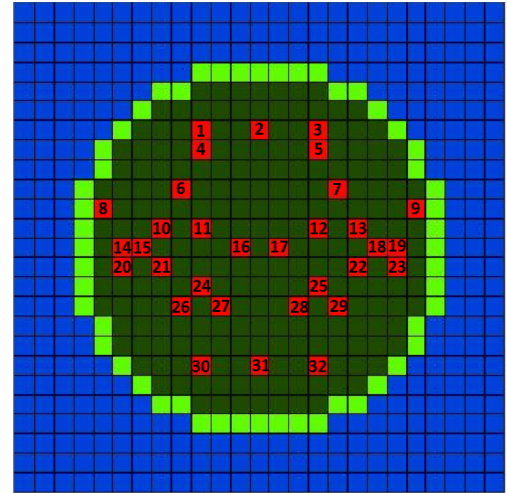


Fig. 3. Test structure position map for the second test wafer design.

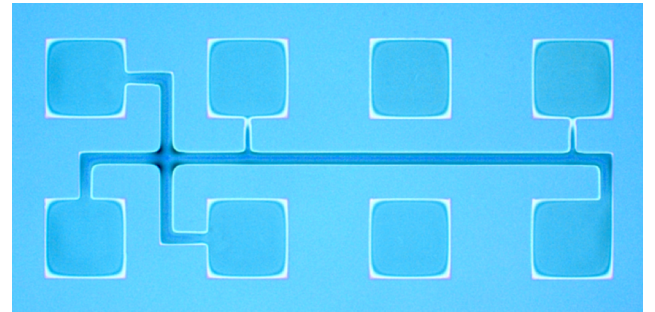


Fig. 4. Cross-bridge test structure from wafer design 2. The designed width of the structure is 20 μm .

Fig. 5 shows the arrangement of resulting array of test chips on a 75 mm silicon wafer. There are 145 measurement points in the complete array, where one Greek cross structure is measured on each chip. As with the previous design, wafers were prepared using SPR350 with a thickness of 2.2 μm and SPR220 with a thickness of 8.4 μm . Wafers of each resist were carbonized at 950 $^{\circ}\text{C}$ and at 1100 $^{\circ}\text{C}$ using the protocol previously described.

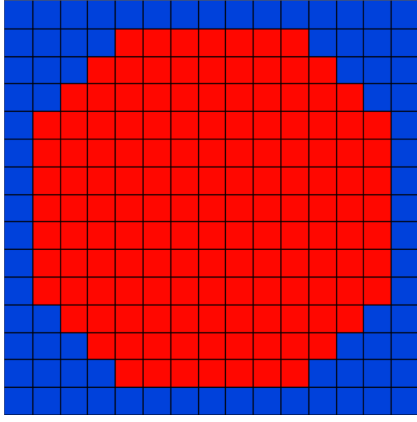


Fig. 5. Test structure position map for the third test wafer design.

D. Carbon Electrodes for Electrochemical Characterisation

The final design used in this investigation (Mask 4) includes circular working electrodes of 200 μm diameter, which are designed for use in a three-electrode electrochemical cell. They are connected to a 5.8 mm by 3 mm contact pad by a 5 μm wide, 5 mm long track, which widens to 20 μm for 5 mm, then 300 μm for 15 mm, as shown in Fig. 6. The contact pad was used to connect the microfabricated electrode to a potentiostat system, via a crocodile clip, to allow electrochemical characterisation.

E. Electrical and Electrochemical Measurements

The initial, on-wafer electrical measurements using mask 1 were made using a manual prober connected to a Keithley 4200 SCS and a standard van der Pauw measurement setup [8]. The best repeatability was obtained using a force current of 1 mA.

The test structures patterned using masks 2 and 3 were specifically designed for measurement using a standard 2 \times 4 probe card on a Suss PA200 semi-automatic probe station. This is connected to an HP4062UX parametric analyser, with an Agilent 3458A digital multimeter for high resolution voltage measurements. Standard test routines developed to measure the same test structure designs fabricated in platinum and tantalum nitride were adapted for use with the carbon structures [5]. A force current of 1 mA was also used in these experiments.

Reversible electrochemistry using electrodes of conductive carbon has previously been reported using a ruthenium based redox reporter [9]. In the current work, cyclic voltammetry of the reduction/oxidation reaction of the ferri/ferrocyanide couple was used to assess if the fabricated carbon would function as an electrode material. An Ag/AgCl reference electrode and a platinum counter electrode were employed. The measurement solution contained 5 mM each of ferri- and ferrocyanide with 100 mM KCl as background electrolyte.

III. MEASUREMENT RESULTS

A. Mask 1 Test Structures

Table I gives the results of sheet resistance measurements at a current on 1 mA on the first test wafer. It is clear that there is significant horizontal variation from top to bottom of the wafer. The wafers were oriented in the boat with the flat at the bottom

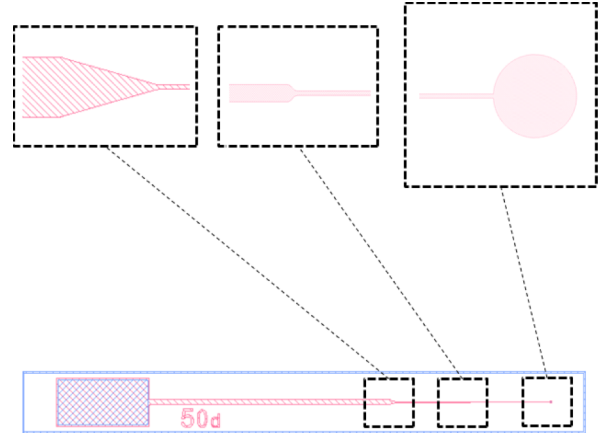


Fig. 6. Electrochemical test structure layout, insets show magnified views of the circular working electrodes and the connecting tracks.

and so this variation may be due to the structures near the top of the wafer (positions 1 and 2) experiencing different gas flow conditions during processing. It would always be noted that these resistance results come from structures where the shape of the structure is quite different to the uniform thickness expected in an ideal van der Pauw structure. Pattern dependent reflow of the structures causes variation of the thickness of the material. Therefore, these results can only be considered to demonstrate that the material is conducting and that there is variation in the material resistance, and/or the cross section of the structures across the wafer.

TABLE I. RESULTS FROM STRUCTURES PATTERNED WITH MASK 1

Sheet Resistance (Ω/\square) \pm Standard Deviation			
Position 1	Position 2	Position 3	Position 4
91.2 \pm 0.13	93.5 \pm 0.05	75.0 \pm 0.02	78.4 \pm 0.02

B. Mask 2 Test Structures

Fig. 7 shows maps of sheet resistance taken from the wafers patterned using mask 2, while Table II shows the results of thickness measurements of the carbon material, made with a Dektak surface profilometer near the centre of each wafer after furnace processing.

TABLE II. DEKTAK THICKNESS MEASUREMENTS OF PYROLYSED CARBON FILMS

SPR350 2.2 μm		SPR220 8.4 μm	
950 $^{\circ}\text{C}$	1100 $^{\circ}\text{C}$	950 $^{\circ}\text{C}$	1100 $^{\circ}\text{C}$
907 nm	773 nm	3340 nm	3197 nm

For both resists, the resistance is significantly lower in the structure treated at the higher temperature. There is variation across the wafer but this is not consistent with the orientation of the wafer flat, which is at the bottom of each map. As the wafers were placed with the flat uppermost in the boat in each case it is difficult to explain why the resistance varies as it does. The averages for each wafer are presented in Table III.

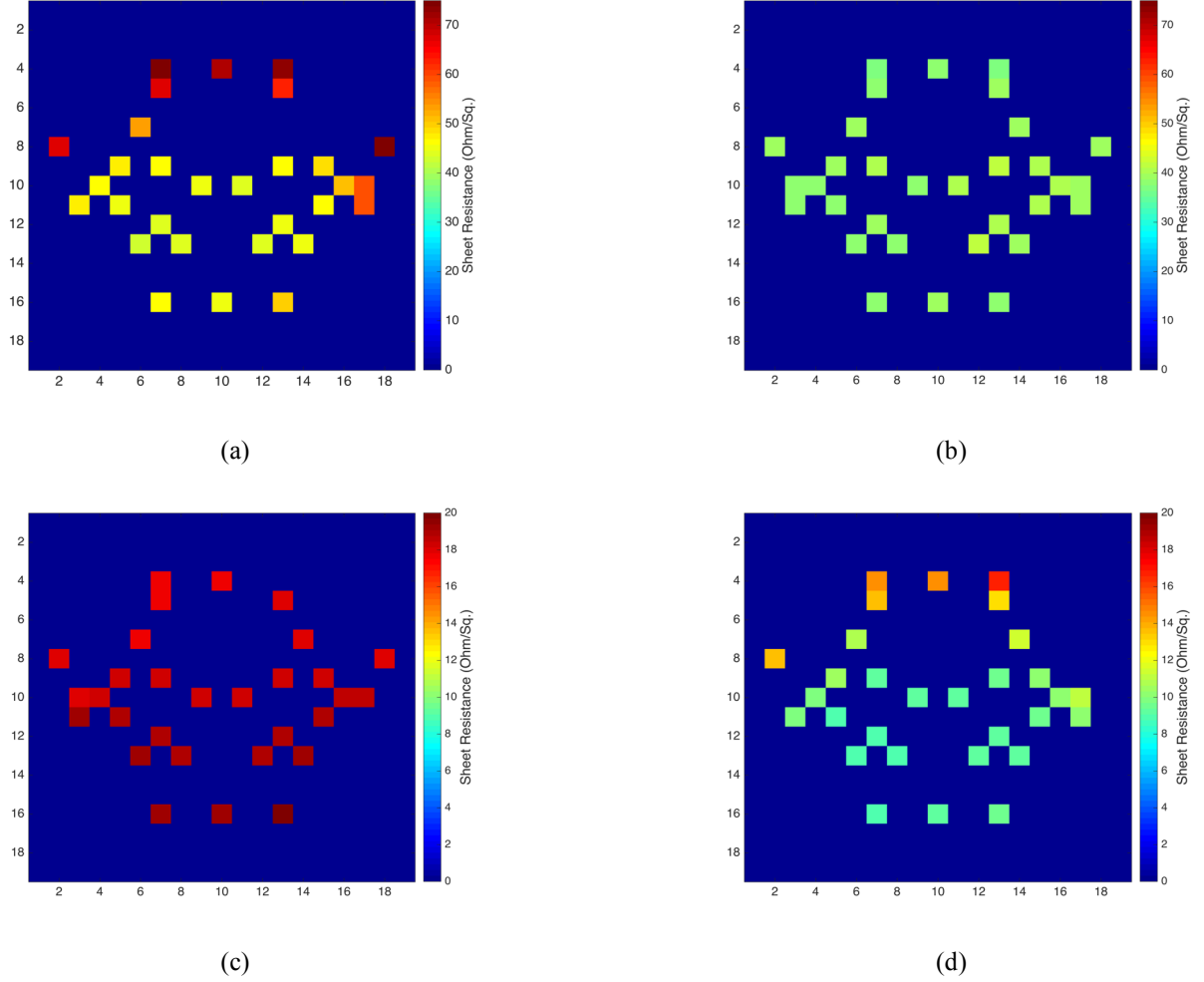


Fig. 7. Wafer maps of sheet resistance measurements patterned using test mask 2, the wafer flat is at the bottom of each image. (a) Structures fabricated from SPR350 photoresist and carbonized at 950 °C. (b) Structures fabricated from SPR350 photoresist and carbonized at 1100 °C. (c) Structures fabricated from SPR220 photoresist and carbonized at 950 °C. (d) Structures fabricated from SPR220 photoresist and carbonized at 1100 °C.

TABLE III. SHEET RESISTANCE MEASUREMENTS OF PYROLYSED CARBON FILMS

SPR350 2.2 μ m		SPR220 8.4 μ m	
950 °C	1100 °C	950 °C	1100 °C
52.71 Ω/\square	39.05 Ω/\square	18.50 Ω/\square	10.58 Ω/\square

C. Mask 3 Test Structures

As before, two wafers of each resist type and thickness were patterned with test structures, and these were pyrolysed at the two different furnace temperatures. Full wafer maps were obtained for wafers processed at 950 °C and are presented in Fig. 8. The averages and ranges for the two different resist types are $68.35 \pm 5.39 \Omega/\square$ for SPR350, and $18.15 \pm 11.99 \Omega/\square$ for SPR220.

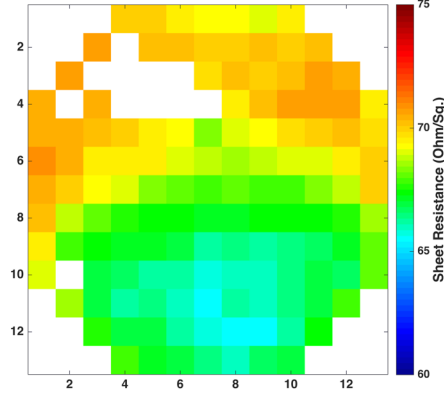
The SPR350 wafer processed at 1100 °C was found to be significantly bowed by the high temperature process, causing problems with vacuum clamping and setting the probe contact

height on the semi-automatic prober. The average and range for the resistance measured on a 6x6 block of structures in the middle of the wafer coated with SPR350 is $32.55 \pm 0.97 \Omega/\square$.

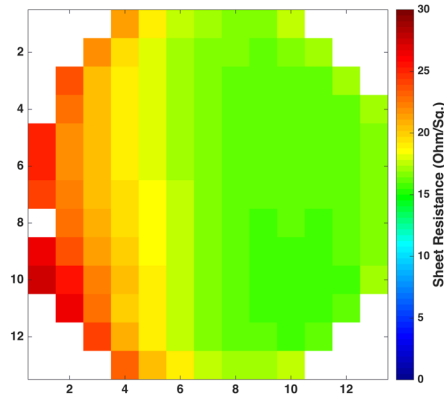
A full wafer map has been obtained for a wafer coated with SPR220 and processed at 1100 °C, and this is presented in Fig. 9. The average and range for the sheet resistance measured with this set of structures is $11.23 \pm 2.21 \Omega/\square$.

While the average results from structures patterned using mask 3 are in broad agreement with those from previous wafers, the variation of the measured resistance across each wafer is still inconsistent. The results from the SPR220 wafer processed at 950 °C are particularly surprising as they show a large variation from left to right across the wafer rather than from top to bottom.

Thickness measurements and profilometry of the carbon material from these wafers are currently unavailable but should be performed in order to properly understand the shrinkage and reflow of the photoresist. Observations during probing suggest more reflow of the thicker SPR 220 resist.



(a)



(b)

Fig. 8. Wafer maps of sheet resistance measurements patterned using test mask 2, the wafer flat is at the bottom of each image. (a) Structures fabricated from SPR350 photoresist and carbonized at 950 °C. (b) Structures fabricated from SPR220 photoresist and carbonized at 950 °C.

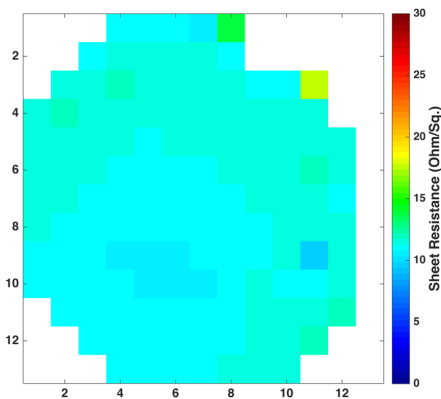


Fig. 9. Wafer map of sheet resistance measurements from a wafer coated with SPR220 photoresist pyrolysed at 1100 °C.

D. Electrochemistry Measurements (Mask 4)

Fig. 10 shows typical cyclic voltammograms of the redox reaction of the ferri/ferrocyanide couple recorded using the electrodes fabricated with the SPR220 photoresist. A triangular voltage signal is applied between the working and Ag/AgCl reference electrode with a ramp rate of 100 mV s⁻¹. The plot shows the current passed between the counter and working electrodes. The voltammogram clearly shows the redox reaction although with a relatively resistive background. This is caused by the long, thin track leading to the electrode and is visible in the high peak separation of oxidation and reduction reactions. As can be expected from the previous measurements of the sheet resistances, the carbon pyrolysed at 1100 °C is the less resistive.

Fig. 11 shows a comparison of the SPR220 and SPR350 resists, both pyrolysed at 950 °C. The voltammogram recorded using the electrode made from the thinner resist SPR350 is more resistive with an even higher peak separation. The thinner film increases the resistance of the track to the electrode, resulting in higher *IR* drop, which again agrees with the previous conductivity measurements. Nevertheless, in both cases, the carbon functions as an electrochemical electrode thus proving the fabrication concept.

IV. CONCLUSIONS

This work has confirmed that conducting carbon patterns suitable for electrodes for electrochemical measurements can be fabricated from standard photoresists. Sheet resistance test structures have been applied to the characterization of thin conductive carbon films produced by high temperature carbonization of positive photoresist patterns. The results indicate significant variation across the wafer, which was initially thought to be associated with the orientation of the wafer in the furnace. However, full wafer map results show that this is not the complete story and therefore further work is required to properly understand the observed results.

Preliminary thickness measurements show more variation in the degree of shrinkage of features with temperature in structures fabricated from thinner SPR350 resist. These results come with the significant caveat that the variation of thickness across the wafer has not been studied. In addition, microscope images of test structures suggest that there is significant pattern dependent variation of the feature thickness and apparent distortion of the structures. One result of the reflow of the photoresist is to distort the shape of Greek cross test structures such that the measured “sheet resistance” can only be considered indicative of the variation of resistance across the wafer. For example, it would not be possible to use results from the cross on an electrical linewidth test structure to obtain the correct critical dimension as there would be significant differences in the thickness of the conducting material.

Preliminary results indicate that this material is capable of being used to fabricate working electrodes for use in electrochemical sensors. Improvements to the design will be important if they are to be applied successfully. For example, reducing the series resistance by increasing the width of connecting tracks and better defining the electrode area through patterned passivation are two essential improvements.

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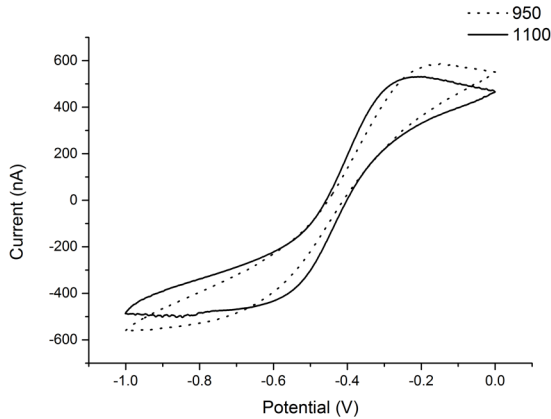


Fig. 10. Cyclic voltammetry results for carbon electrodes fabricated from SPR 220 photoresist carbonised at 950 and 1100 °C.

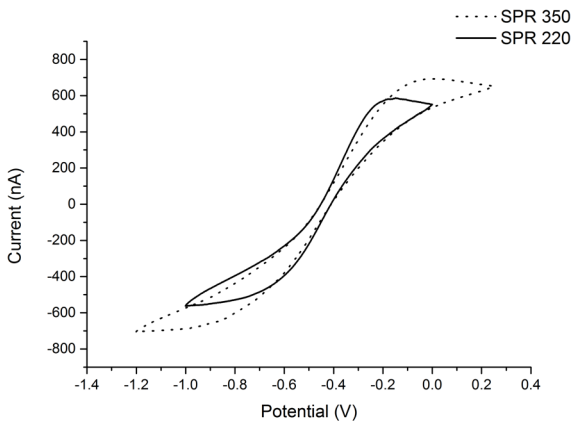


Fig. 11. Cyclic voltammetry results for carbon electrodes fabricated from SPR 350 and SPR 220 photoresist carbonised at 950 °C.